EXHIBIT 9

Performance of a new cationic bleach activator on ahydrogen peroxide bleaching system

Sang-Hoon Lim,a Nevin igdem G¨1rsoy,b Peter Hausera,* and David Hinksa

Email: peter_hauser@ncsu.edu

bDepartment of Textile Engineering, Istanbul Technical University, Istanbul 80191,Turkey

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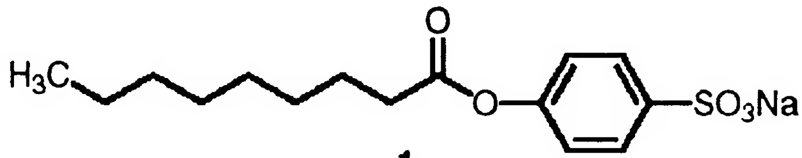
Abstract

The performance of a cationic bleach activator, N-[4-(triethylammoniomethyl)benzoyl]caprolactam chloride, was evaluated in a hot peroxide bleaching process. The effect of time, temperature and the concentrations of hydrogen peroxide and activator on the bleaching of cotton fabric was investigated using a central composite experimental design. Temperature was found to be the most significant parameter. By adding the cationic activator it was possible to achieve a level of whiteness comparable to a typical commercial bleaching system but under relatively mild conditions of time and temperature. As a consequence, chemical damage to the fabric could be reduced. The effect of the cationic bleach activator was compared to that of an anionic activator, nonanoyloxybenzene sulphonate. The cationic activator was superior to the anionic activator in bleaching the fabric under the optimised conditions used in the study.

1. Introduction

Cotton fibres contain yellowish impurities which detract from the inherent white colour of the fibre. Unless the fibres are to be dyed deep or dark shades, bleaching is required to remove these natural colorants. Hydrogen peroxide is the most widely used oxidant for this purpose. Bleaching with this material is traditionally carried out under alkaline conditions at temperatures around 95 °C. This involves high energy costs and can also give rise to fibre damage.

Bleach activators are added to promote the oxidation potential of alkaline hydrogen peroxide. These generate peracids, which allow bleaching to be conducted at lower temperatures and for a reduced time, resulting in energy savings and less fabric damage. Among the bleach activators recently developed for incorporation into household laundry detergents, the most common are nonanoyloxybenzene sulphonate (NOBS) (1) and tetra-acetylethylenediamine (TAED) (2). Following from the increasing awareness of the textile industry to the benefits of activated peroxide bleaching systems, a number of reports have described the use of these two materials [1-5].



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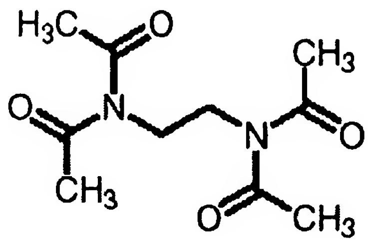

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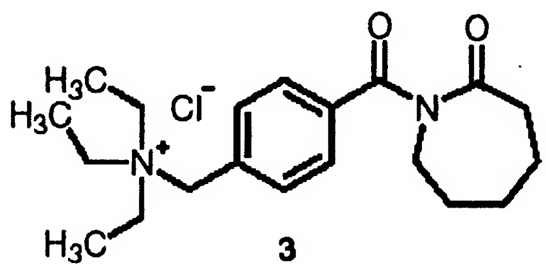
Other cationic bleach activators have also been recently reported [6]. These potentially offer increased affinity for the negatively charged surface of cotton in water, as a result helping to minimise hydrolysis in the bleach solution and maximising oxidation at the relevant sites on the substrate. However, no studies have yet been reported on the behaviour of cationic bleach activators in the hot bleaching of textiles. The present study describes the evaluation and optimisation of a novel cationic bleach activator, N-[4-(triethylammoniomethyl)benzoyl]caprolactam chloride (3), using a modification of a typical hot peroxide bleaching system offered by a leading US supplier of textile chemicals.



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Experimental

Materials

The fabric used was single jersey circular-knitted greige cotton (175 g/m2, 18/1 Ne OE 100%). Tap water was used for the bleaching and washing processes.

The cationic bleach activator 3 was synthesised and purified by the procedure reported previously [6]. NOBS 1 was kindly provided by the Procter and Gamble Company(Cincinnati, USA). The surfactant (Pat-Terge 378 EC), the dispersing agent (Dispersant 2000) and the stabiliser (Stabiliser 128) were kindly provided by Yorkshire Americas, Inc. Other chemicals were purchased from Aldrich Chemical Company (Milwaukee, USA) and Fisher Scientific Company (Suwanee, USA) and

were used without further purification.

Hot bleaching

The bleaching solutions each contained surfactant,dispersing agent, stabiliser, hydrogen peroxide (35%),sodium hydroxide and the bleach activator 3. For all bleachings the quantities of surfactant, dispersing agent,sodium hydroxide and stabiliser were those suggested in a commercial recipe. All bleachings and hot washings were carried out in a laboratory IR dyeing machine (Ahiba Nuance, Datacolor International) at a liquor ratio of 20:1 .

After addition of fabric (10 g) to a 250 ml stainless steel beaker containing the bleach solution (200 ml), the temperature was raised to the target bleaching temperature.After the specified bleaching time the bath was then cooled to 50 ℃. The fabric was removed and squeezed using a laboratory padder (Warner Mathis AG). It was washed in water (200 ml) at 95℃ for 10 min and then cooled to 50 ℃. The bleached fabric was finally rinsed thoroughly with tap water and air dried. During both bleaching and hot washing the rate of heating and cooling was 3 ℃/min.

Measurement of whiteness

The CIE whiteness index (WI) was calculated for each fabric using AATCC Test Method 110-1995 [7]. Reflectance values were measured on a Datacolor Spectraflash SF 600 Plus-CT using illuminant D65, large area of view, specular included and CIE 1964 supplemental standard 10 observer. Each sample was folded twice to give opacity and the whiteness index was averaged over four separate points on the surface.

Degree of polymerisation of cotton fabrics

The fluidity of the cotton fabric was measured according to AATCC Test Method 82-1996 [7]. The cuen fluidity (F) was converted to the degree of polymerisation (DP) using Eqn 1 [8].

$$DP = 2032\left(\log_{10}\frac{74.35+F}{F}\right)-573 \qquad (1)$$

Statistical design of experiments

The bleaching experiments were conducted using central composite design (CCD). The experimental design and statistical analysis were performed using a statistical software, Design-Expert (v. 6.0.8), supplied by Stat-Ease, Inc. (Minneapolis, MN). Four factors potentially affecting bleaching performance were evaluated, namely time, temperature and the concentrations of hydrogen peroxide and activator. The CCD contains five levels for each factor, the coded levels and actual values being shown in Table 1. The parameter to be optimised was the value of CIE WI for the bleached fabrics. The total number of bleaching experiments was 30, including 16 at factorial points, eight at star points and six replications at the centre point. The pattern of the levels of the four factors is shown in Table 2, along with the whiteness values resulting from the individual experiments.

Table 1 Coded and actual levels of the design factors

Factor symbol	Factor	−2	−1	0	+1	+2
X_1	3[a] (g/200 ml)	0	0.2	0.4	0.6	0.8
X_2	H_2O_2 (g/200 ml)	1.0	1.25	1.5	1.75	2.0
X_3	Time (min)	10	15	20	25	30
X_4	Temp. (° C)	80	87.5	95	102.5	110

a Bleach activator

Table 2 Central composite design for the hot bleaching

No.	X_1	X_2	X_3	X_4	Y (CIE WI)
1	−1	−1	−1	−1	64.82
2	1	−1	−1	−1	67.73
3	−1	1	−1	−1	67.67
4	1	1	−1	−1	70.53
5	−1	−1	1	−1	66.62
6	1	−1	1	−1	69.87
7	−1	1	1	−1	69.12
8	1	1	1	−1	70.91
9	−1	−1	−1	1	69.76
10	1	−1	−1	1	72.47
11	−1	1	−1	1	73.62
12	1	1	−1	1	76.64
13	−1	−1	1	1	73.01
14	1	−1	1	1	74.72
15	−1	1	1	1	75.43
16	1	1	1	1	76.32
17	−2	0	0	0	66.71
18	2	0	0	0	72.10
19	0	−2	0	0	69.39
20	0	2	0	0	73.24
21	0	0	−2	0	69.95
22	0	0	2	0	72.09
23	0	0	0	−2	66.28
24	0	0	0	2	76.57
25	0	0	0	0	71.40
26	0	0	0	0	72.06
27	0	0	0	0	71.83
28	0	0	0	0	71.95
29	0	0	0	0	70.24
30	0	0	0	0	72.04

Results and Discussion

Statistical analysis

The CCD contains five levels for each factor. This number of levels permits the design to generate sufficient data to fit the quadratic model. After analysis of variance (ANOVA) for the quadratic model, including all model terms, those having probability values (p-values) greater than 0.05 were eliminated since they were not statistically significant at the 95% confidence level. The ANOVA data for the significant model terms are given in Table 3 and are based on the use of coded levels for each factor. The model p-value of <0.0001 confirms that the model is significant.The first term, a constant, is referred to as the intercept.The four terms following (X1 to X4) are the main factors affecting the response, their values indicating the contribution of each factor [9]. It is seen that temperature had the greatest effect, followed in turn by the concentration of bleach activator (3), the peroxide in describing the nonlinearity of the response. It can be seen that the influence of bleach activator concentration on fabric whiteness is nonlinear. Also, the term X2 X3 shows that there is a relationship between hydrogen peroxide concentration and time during the process.

Table 3 ANOVA for the quadratic model (R^2 = 0.9704) after exclusion of insignificant terms

Model terms	Estimated coefficient	Standard error	p-value[a]
Constant	71.55	0.14	
X_1	1.25	0.12	<0.0001
X_2	1.21	0.12	<0.0001
X_3	0.71	0.12	<0.0001
X_4	2.72	0.12	<0.0001
X_1^2	−0.47	0.11	0.0003
X_2X_3	−0.38	0.15	0.0177

a Model p-value = <0.0001

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The lack-of-fit statistic was used to test the adequacy of the model obtained and the p-value was found to improve from 0.7102 to 0.7719 after exclusion of statistically insignificant terms. The lack of fit was not significant, since the p-value of 0.7719 exceeded the 0.05 threshold value. In addition, no abnormality was observed from the diagnoses of residuals. It could therefore be concluded that the model was statistically sound.

The quadratic model predicting CIE WI in terms of actual values of different factors within the scope of the experiments is shown in Eqn 2.

$$\begin{aligned} \mathrm{WI} = {} & 13.46 + 15.67X_1 + 10.94X_2 + 0.60X_3 \\ & + 0.36X_4 - 11.80X_1^2 - 0.31X_2X_3 \end{aligned} \qquad (2)$$

This model was used for prediction of the response (CIEWI) throughout the entire experimental volume evaluated.

Effect of bleaching parameters on whiteness of fabric

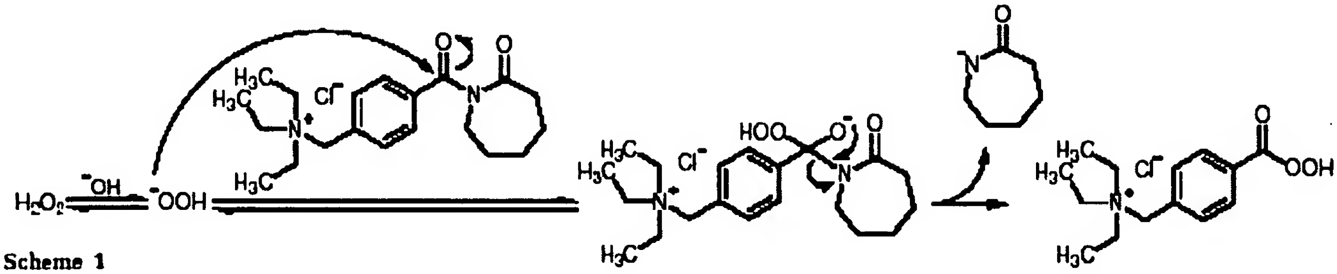
Bleach activation may be defined as the chemical reaction that converts the kinetically less potent bleaching species to one which is kinetically more powerful. As shown in Scheme 1, in the presence of alkali and hydrogen peroxide the bleach activator produces a peracid, which gives a potentially more effective bleaching system than alkaline hydrogen peroxide alone. The peracids generated by cationic bleach activators themselves contain cationic groups, and these potentially increase their affinity forcotton in an aqueous environment. This combination of enhanced affinity and increased oxidation potential leads to improved bleaching performance on cotton.Table 3 ANOVA for the quadratic model (R2 = 0.9704) after exclusion of insignificant terms Model Estimated Standard terms coefficient error p-valuea The effect of bleaching parameters on the whiteness of bleached cotton is illustrated in Figure 1, in which CIE WI is shown as contour lines and the levels of the parameters not shown for each plot are at their central point (see Table 1 for zero level). It may be observed that within the ranges investigated the whiteness was strongly dependent on bleaching temperature but less so on the time of bleaching.

The performance of a bleaching system has previously been shown to improve as the concentration of hydrogen peroxide or peracid increases [10]. In the present system,which contained both hydrogen peroxide and peracid, the bleaching performance became better as the concentration of either or both components increased. It therefore appears that the two components have an additive effect. It is well known that increased temperature gives a higher rate of bleaching [11]. As shown in Figure 1, the temperature had the largest effect on the whiteness of the cotton. If hydrogen peroxide is used to bleach cotton at room temperature it typically requires at least an overnight dwell time. An increase in temperature and the addition of a bleach activator can improve bleaching performance over a greatly reduced bleaching time [12,13].

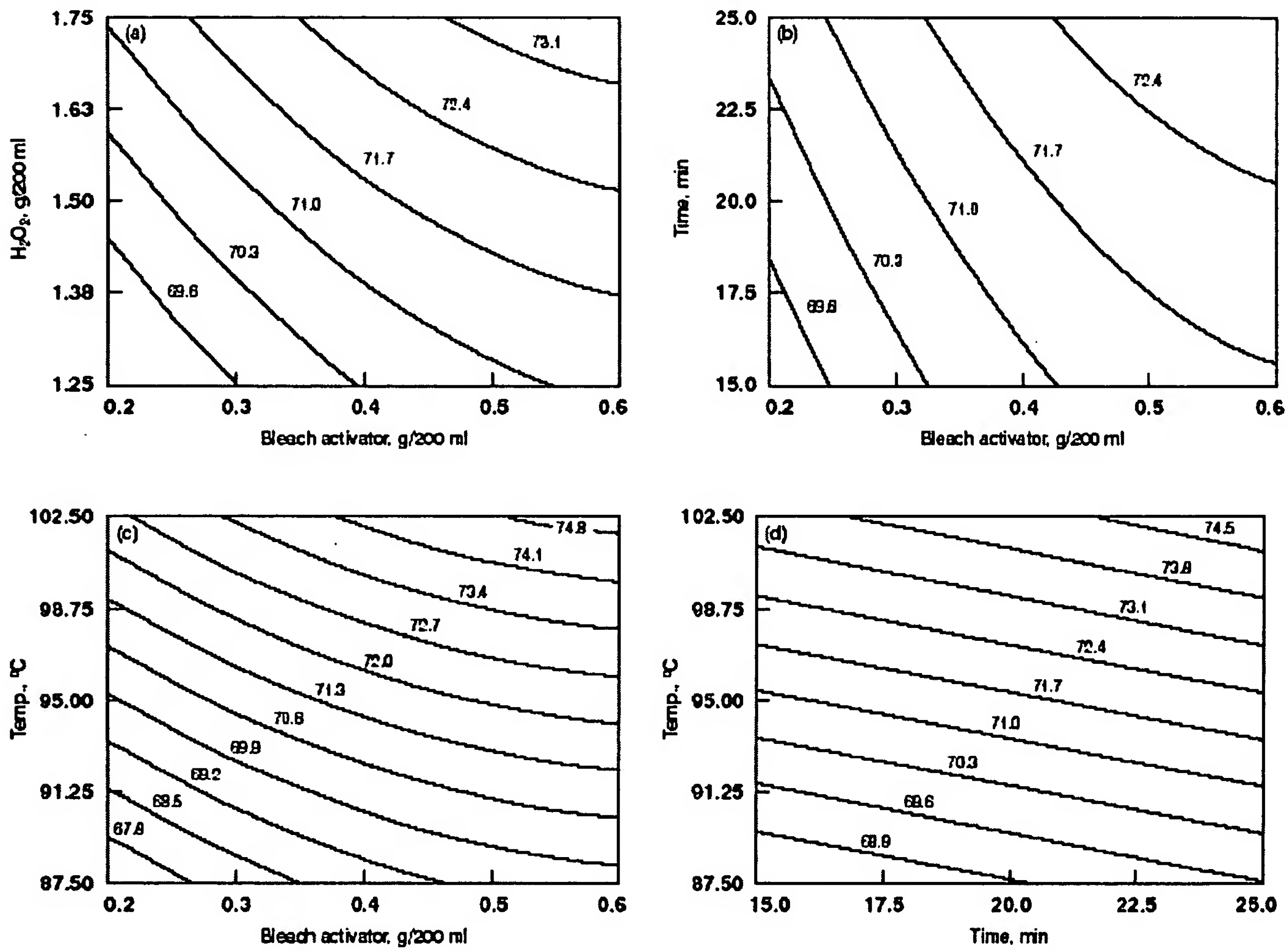
Optimisation of the process

The experimental design software was used to obtain an optimal recipe for the bleaching system. The objective was to establish a recipe which provided a similar whiteness value (75.91) to that given by the original commercial recipe but with a reduced time and temperature, the other factors being kept constant. The components of the commercial and optimised recipes are given in Table 4.

By way of comparison, cotton was bleached using a similar optimised recipe, except the cationic bleach activator 3 was replaced by a molar equivalent quantity of NOBS 1. The CIE WI and DP values for each recipe were calculated and are shown in Table 5, from which it is seen that the measured and predicted whiteness values for the cationic bleach activator were in good agreement. Furthermore, the addition of the cationic bleach activator provided comparable whiteness value to the commercialsystem in reduced time and at lower temperature. This is beneficial in terms of energy saving and reduced damage to the fabric, as the results in the table show. When a drop of water was placed on fabrics bleached using the cationic bleach activator system and the commercial bleach, respectively, no difference in wettability was observed.



Scheme 1



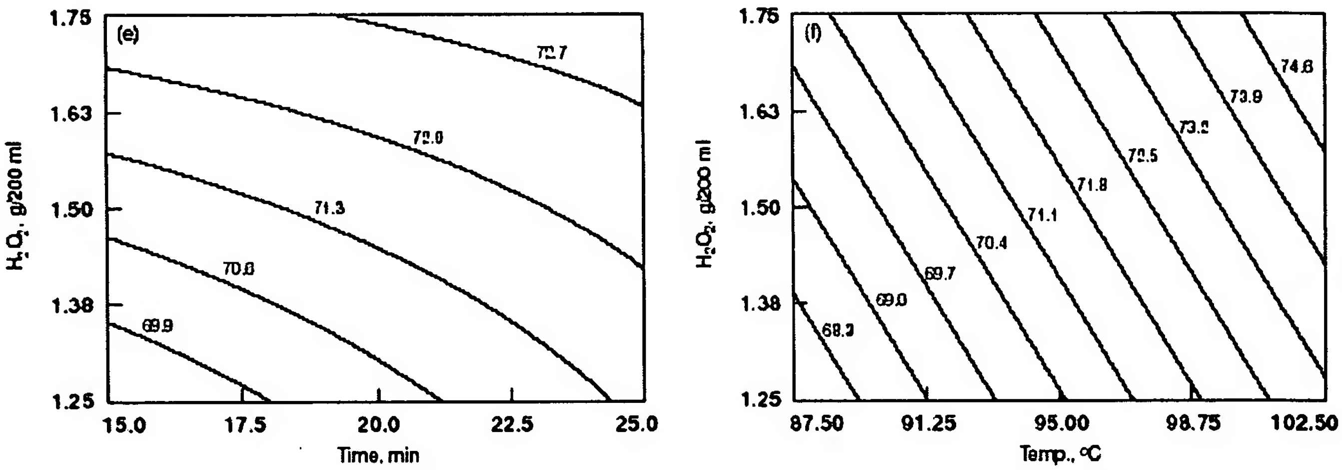


Figure 1 Effect of bleaching parameters on whiteness of cotton; note: contour lines represent CIE WI and the levels of parameters not shown for each plot are at their centre point (zero level in Table 1)

Table 4 Commercial and predicted optimised bleach recipes

Recipe[a]	Bleach activator **3** (g/200 ml)	H_2O_2 (g/200 ml)	Time (min)	Temp. (°C)
Commercial		1.71	25.0	110.0
Optimised	0.6	1.71	18.3	102.5

a The quantity of surfactant (0.75 g/l), dispersing agent (1.25 g/l), sodium hydroxide (50%, 3 g/l) and stabiliser (0.25 g/l) were identical for both bleach recipes

Table 5 Whiteness and DP values

	CIE WI		
System	Predicted	Measured[a]	DP[b]
Commercial		75.91	2779
Bleach activator **3**	75.91	75.56	2984
NOBS		73.02	3068

a CIE WI before bleaching = -1.24
b DP before bleaching = 3302

In addition, the cationic bleach activator in this bleaching system produced a higher whiteness level on the abric than did NOBS, possibly because the cationic bleach activator had a higher affinity for the negatively charged cotton than an anionic bleach activator such as NOBS.Further work will be needed to confirm this.

Conclusions

In the presence of hydrogen peroxide and alkali, bleachactivators generate peracids, which are more potentoxidants. In this study a cationic bleach activator 3 wasemployed to assist a hydrogen peroxide hot bleachingsystem. It was observed that temperature had the greatestinfluence on the whiteness of cotton fabric, followed inturn by the bleach activator concentration, hydrogen peroxide concentration and time. The predicted and measured whiteness values from the optimised recipe for the cationic bleach activator were in close agreement,confirming the validity of the quadratic model used.

By the addition of the cationic bleach activator 3 to a conventional hot bleaching system, it was possible to obtain a similar level of whiteness at lower temperature and reduced time while maintaining wettability. In regard to fibre damage after bleaching, the cationic bleach activator system gave less chemical damage than the conventional bleaching system, as indicated by the high residual degree of polymerisation. This activator may therefore be beneficial when bleaching fibre blends containing delicate components, for example cotton/wool blends, in which the wool is prone to damage in the hot alkaline conditions.

In this study a typical commercial process has been modified by the simple addition of a novel cationic bleach activator. It is possible that a further reduction in processing time and temperature might be achieved, for example, by the choice of stabiliser and further modification of the structure of the cationic bleach activator.

References

1. J Y Cai, D J Evans and S M Smith, AATCC Rev., 1 (2001) 31.
2. J Wang and N M Washington, AATCC Rev., 2 (2002) 21.
3. A J Mathews, Book of Papers, Proc. AATCC Int. Conf. Exhib., Atlanta, USA (1997) 462.
4. J Y Cai, F J Harrigan and S M Smith, Book of Papers, Proc. AATCC Int. Conf. Exhib., Charlotte, USA (1999) 134.
5. S J Scarborough and A J Mathews, Text. Chem. Colorist Am. Dyestuff Rep., 32 (3) (2000) 33.
6. A D Willey, G S Miracle, K L Kott, M E Burns, G M A Baillely, N Guedira, F E Hardy, L F Taylor and M R Sivik, US5686015 (Procter and Gamble, USA; 1997).
7. AATCC Technical Manual, Vol. 75 (Research Triangle Park: AATCC, 2000).
8. A Bleacher's Handbook (Houston: Solvay Interox, 1981) 57.
9. R J del Vecchio, Understanding Design of Experiments: A Primer for Technologists (Cincinnati: Hanser/Gardner Publications Inc, 1997).
10. A P James and I S Mackirdy, Chem. Ind. (London, UK) (1990) 641.
11. W S Hickman, in Cellulosics Dyeing, Ed. J Shore (Bradford: SDC, 1995) 117.
12. N G??rsoy, S H Lim, D Hinks and P Hauser, Text. Res. J., in press.

13. N G??rsoy, A El-Shafei, P Hauser and D Hinks, Book of Papers, Proc. AATCC Int. Conf. Exhib., Greenville, USA (2003) 216.

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